Tracing redox at depth using apatite?

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The redox state ($f_{O_2}$) of magmatic systems is a key variable that influences crystallization and degassing processes, and determines among other things, ore metal ratios in porphyry ore deposits. Apatite [Ca$_5$(PO$_4$)$_3$(F, Cl, OH)] is a ubiquitous, resistant mineral in magmatic systems and can contain up to several thousand ppm of S and Mn [1, 2]. Recently, it was reported that Mn contents in some natural apatites correlate negatively with $f_{O_2}$, possibly allowing for Mn-in-apatite to be used as an oxybarometer [2]. Sulphur in apatite is another potential $f_{O_2}$ proxy, considering that S is thought to be incorporated in apatite as sulphate (S$^{6+}$) [3] and, therefore, the S content of apatite should decrease with decreasing $f_{O_2}$; i.e. with lower S$^{6+}$/S$^{2-}$ in the melt. In this study, we are experimentally testing the S-in-apatite and Mn-in-apatite oxybarometers.

Apatite is crystallized from rhyolitic melt at 800°C, 200 MPa, and $f_{O_2} = \Delta$NNO+1, by seeding the melt with <2μm diameter apatite crystals. Run durations of 10 days yield homogeneous apatite crystals up to 25μm in diameter. Run products are analysed using EPMA. Nernst-type partition coefficients (±1σ) are $D_{\text{S\ Ap/Melt}} = 7.9 \pm 2.3$ and $D_{\text{Mn\ Ap/Melt}} = 8.4 \pm 5.7$. We use anhydrite or pyrrhotite to monitor $f_{S_2}$ since it has been reported that $f_{S_2}$ affects $D_{\text{S\ Ap/Melt}}$ [1]. However, this correlation has never been calibrated experimentally.

Our new data indicate that the equation provided by Parat et al. [1] for the correlation between the S content in the melt and the S content in apatite underestimates the $D_{\text{S\ Ap/Melt}}$ by a factor of ~1.7. We suggest that this may simply be related to the lack of data at lower S contents in the melt (< 130 ppm). More puzzling is that the Mn-in-apatite oxybarometer developed by Miles et al. [2], which was calibrated using natural samples exclusively, predicts a $f_{O_2}$ that is ~2 orders of magnitude more reducing than the intrinsic $f_{O_2}$ of our experiments. Additional inconsistences arise when comparing the Miles et al. [2] model to the experimental Mn-in-apatite data from Mathez and Webster [4] at lower $f_{O_2}$ ($\Delta$NNO-2 to +0). The observed discrepancies between our data and published studies highlight the critical need for additional experimental data that fully constrain $D_{\text{S\ Ap/Melt}}$ and $D_{\text{Mn\ Ap/Melt}}$ over a wide range of $f_{O_2}$, $f_{S_2}$ and melt compositions.